JP,2002-306976,A [DETAILED DESCRIPTION]

## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The semiconductor manufacturing industry, the pharmaceutical industry, food stuff industry for which this invention uses deionized water, It is related with an electric type device for producing deionized water provided with the porosity ionic exchanger, deionization module, and deionization module which are used suitably for the electric-type deionization liquid manufacturing installation used by manufacture of various kinds of industry, such as plant and a research institute, or honeydew, juice, wine, etc., etc.

[0002]

[Description of the Prior Art]The electric type device for producing deionized water put in practical use from the former, Fill up with mixed-ions exchange resin of an anion exchange resin and cation exchange resin the crevice fundamentally formed by cation exchange membrane and anion exchange membrane as an ionic exchanger, and it is made it with a desalting room, While making the ion-exchange resin concerned pass processed water, a direct current is made to act on rectangular directions to the flow of processed water via said both ion-exchange membranes, and deionized water is manufactured, eliminating processed underwater ion electrically in the retentate which is flowing into the outside of both ion-exchange membranes. Since processed underwater impurity ion is electrically removed by such operation, deionized water can be obtained continuously, without completely performing reproduction according filled ion-exchange resin to a drug solution.

[0003]Since the reproduction by a drug solution is unnecessary in an electric type device for producing deionized water, the operating cost is determined by amount of used electricity. If the rectification loss at the time of changing exchange into a direct current is removed, the power consumption in an electric type device for producing deionized water is expressed with the direct-current x voltage between two electrodes. Here, a direct current is determined by the kind and the treated water quality demanded of the quantity of the ion which processed water contains, and ion. Namely, in an electric type device for producing deionized water, it is necessary to discharge continuously the ion caught by ion-exchange resin in the desalting room to the retentate side by electric migration, and ion is migrated -- making -the current more than [required ] fixed is indispensable in order that an electric type device for producing deionized water may demonstrate the performance normally. Therefore, in the usual case, in the electric type device for producing deionized water, constant current operation holding the fixed current value which exceeds a required minimum current value on the operating condition is performed. On the other hand, voltage is determined by the electrical resistance between said two electrodes, and it depends for it on the performance of the ion-exchange membrane and ion-exchange resin which are used for an electric type device for producing deionized water greatly. That is, this electrical resistance is total of the electrical resistance by the electrode chamber, enriching chamber, and desalting room which were allocated between two electrodes.

Inter electrode distance and an operating temperature The concentration and the kind of ion which are contained in electrode water and retentate, [fixed then] The contact resistance in the interface of an ion-exchange membrane, the kind of ion-exchange resin and the kind of counter ion of the ion exchange group, the filling method (a single flooring or a mixed bed) of ion-exchange resin, and also these electrical resistance [all] components affects it.

Although the concentration and the kind of ion which are contained in electrode water and retentate among said electrical resistance components are determined by the water quality and the quality of treated water demanded of processed water, it depends for other elements on the performance and the directions for the ionic exchanger used for an electric type device for producing deionized water. [0004]However, in the conventional electric type device for producing deionized water, Minimization of said electric resistance value was not considered so that the general-purpose article which had spread from old might be diverted as it is and the ion-exchange resin with which a demineralization module is filled up might reduce the operating cost of an electric type device for producing deionized water. Namely, in the conventional electric type device for producing deionized water. Generally as ion-exchange resin, to the copolymer of styrene and divinylbenzene (DVB). It fills up with the spherical thing with a diameter of about 0.2-0.5 mm produced by introducing a sulfonic group (R-SO<sub>3</sub> - H<sup>+</sup>) as a cation exchange group, and introducing a quarternary-ammonium-salt group (R-N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>) as an anion

cation exchange group, and introducing a quarternary-ammonium-salt group  $(R-N^+R_1R_2R_3)$  as an anion exchange group. In this case, transfer of the current transfer in ion exchange resin particles, i.e., an electron, and ion, In an ion-exchange-resin-particles interface to being carried out by low resistance via the ion exchange group which exists uniformly and densely in polymer gel, On the occasion of ion and electron transfer, in the case of ion, the underwater migration distance of this ion, since the electron transport pathway through the hydrogen bond between water molecules is long in the case of an electron, and is spherical to it and the touch area of particles is small, the flow of ion concentrates on this contact surface, becomes the hindrance factor of current transfer, i.e., the cause of electrical resistance, and serves as a key factor of the electrical resistance of ion-exchange resin origin. [0005]The conventional electric type device for producing deionized water needs considerable time and

labor for manufacture in order to fill up a deionization module with general-purpose ion-exchange resin. Carrying out two or more sheet lamination adhesion of the end of sandwich shape using adhesives, especially the assembly of the deionization module which forms a desalting room must be uniformly filled up with the ion-exchange resin which carried out humidity, and manufacture takes considerable skill to it and it is hard to automate it. Even when not using adhesives, the handling of ion-exchange resin which carried out humidity is difficult.

[0006]For example, it has the porous structure which combined ion-exchange resin using binding-material polymer as what solves these, the porosity ionic exchanger (JP,8-252579,A.) holding specific water permeability JP,10-192716,A etc. join using adhesives and form an anion exchanger and a cation exchanger in one, And the desalting room structure which becomes unnecessary [ the frame or ion-exchange membrane which made specific structure the dipping part and the liquid penetrating sealed part ] (JP,2000-218137,A), In [ form porous structure in the surface portion of cation exchange membrane or anion exchange membrane, and ] the surface portion of the porous structure concerned, Cation exchange membrane and anion exchange membrane are contacted, and the porous part of porous structure is made into the channel where processed water circulates, and the thing (JP,11-192491,A) aiming at simplification of structure, etc. are proposed.

[0007] However, when using as packing of a deionization module the porous-structure object indicated to JP,8-252579,A etc., the problem of the device manufacture which accompanies uniform restoration of the aforementioned granular ion exchange resin improves. Join together using binding-material polymer and the granular ion exchange resin conventionally filled up with this porous-structure object into the deionization module as it was However, [a porous-structure object and nothing]. The new process on

porous-structure object manufacture of introducing an ion exchange group depending on the case is needed also for the binding-material polymer part, it changed to the simplification like a device assembler, and manufacture of a deionization module filler is complicated. It cannot be said that this porous-structure object is enough as an improvement of the high electric resistance originating in restoration of above-mentioned granular ion exchange resin. Namely, even when an ion exchange group does not exist in a joint polymer portion or it exists in these porous-structure objects, the parent of binding-material polymer and the structure of an ion exchange group differ from an ion-exchange resin portion, and. The existing density of an ion exchange group is low compared with an ion-exchange resin portion, and it is difficult for the whole to consider it as a homogeneous ionic exchanger. For this reason, the problem of the ion in an above-mentioned packed bed or the heterogeneity of an electronic transition is solved, and it cannot be said that reduction of the electrical resistance of an ionic exchanger packed bed and the efficient discharge to the enriching chamber of prehension ion are enough. [0008]

[Problem(s) to be Solved by the Invention] Thus. [whether each conventional porosity ionic exchanger is the integral-construction thing which combined ion-exchange resin of particle state by binding-material polymer, and ] There is no concrete statement about porous structure, and Kabeuchi of macro pore which is manufactured by a high disperse phase emulsion polymerization and which is connected mutually, and macro pore does not have what indicated the thing of open cell structure which has the meso pore used as the channel of water. Although it is manufactured by JP,4-49563,B according to a high disperse phase emulsion polymerization and the porous polymer which heightened the absorptance of aquosity acid or organic acid is indicated, this porous polymer has swelling and too high liquid absorption capability, and is not suitable for manufacture of deionized water.

[0009]Therefore, the purpose of this invention has a specific open cell structure, and pore volume and specific surface area boil it markedly, and it provides a big porosity ionic exchanger. Other purposes of this invention are easy to assemble, and provide the deionization module of a simple structure. Other purposes of this invention reduce the voltage at the time of operation, and there are in providing the power-saving type electric type device for producing deionized water which can reduce power consumption.

## [0010]

[0010] [Means for Solving the Problem]A porous body which has a specific open cell structure acquired by this invention persons polymerizing a water-in-oil type emulsion in this actual condition, for example as a result of inquiring wholeheartedly, intensity is held, and pore volume and specific surface area are markedly alike, and find out that it is suitable for an ionic exchanger of an electric type device for producing deionized water since it is large etc., and it came to complete this invention. [0011]Namely, this invention has the open cell structure of having the meso pore whose pitch diameter is 1-1000 micrometers in Kabeuchi of macro pore connected mutually and macro pore, Whole pore volume is 1 - 50 ml/g, an ion exchange group is distributed uniformly and ion exchange capacity provides a porosity ionic exchanger which are 0.5 mg equivalents / more than g dry porous body. This porosity ionic exchanger is an ionic exchanger with a specific open cell structure, and the conventional particle condensation type porous body is a completely different new structure, this especially porous body holding intensity, pore volume and specific surface area can be boiled markedly, and it can enlarge them.

[0012]This invention comes to fill up said porosity ionic exchanger a building envelope formed by

cation exchange membrane sealed at one frame side, and anion exchange membrane sealed at the another side side, and provides a deionization module used for an electric type device for producing deionized water. According to this deionization module, since it can fabricate cylindrical and cutting can use plate-like and an easy polymer material, a porosity ionic exchanger with which space between ion-exchange membranes is filled up is easy to assemble, and it can make it a simple structure, for example. This invention provides an electric type device for producing deionized water provided with said deionization module. This electric type device for producing deionized water can reduce voltage at the time of operation, and can be used as a power-saving type which can reduce power consumption. [0013]

[Embodiment of the Invention] The pitch diameter of the basic structure of the porosity ionic exchanger of this invention is 1-1000 micrometers to Kabeuchi of the macro pore connected mutually and macro pore. It is the open cell structure of having 10-100-micrometer meso pore preferably. That is, an open cell has the meso pore from which macro pore with a pitch diameter of 2-5000 micrometers and macro pore lap, and \*\*\*\* and this lapping portion usually serve as a common opening, and that most is a thing of open pore structure. If open pore structure pours water, the inside of the air bubbles formed by this macro pore and this meso pore will serve as a channel. As for the number of the things of 1-12 pieces and many, the lap of macro pore and macro pore is 3-10 in one macro pore. It is not desirable at the point that on the other hand desalting efficiency will fall by the pressure loss at the time of water flow becoming large if this is used for water treatment as the pitch diameter of meso pore is less than 1 micrometer if the pitch diameter of meso pore is larger than 1000 micrometers, when the structure of a porosity ionic exchanger turns into the above open cell structures, a macro pore group and a meso pore group can be formed uniformly, and compared with a particle condensation type porous body which is indicated to JP.8-252579. A etc., pore volume and specific surface area can be boiled markedly, and can be enlarged. For this reason, if this is used as an ionic exchanger of an electric type device for producing deionized water, desalting efficiency improves remarkably and is dramatically advantageous. [0014] This porosity ionic exchanger is 1-50ml/g in whole pore volume. Since the amount of water flow per unit sectional area becomes it small that whole pore volume is less than 1 ml/g and throughput declines, it is not desirable. On the other hand, if whole pore volume exceeds g in 50ml/, since the rate that skeletal parts, such as polymer, occupy falls for example, and the intensity of a porous body falls remarkably, it is not desirable. In the conventional porosity ionic exchanger, since whole pore volume is at most 0.1 - 0.9 ml/g, it can use the thing of the high pore volume of 1 which is not in the former exceeding it - 50 ml/g, and high specific surface area. As for this porosity ionic exchanger, when the thickness is 10 mm, it is preferred that water transmission rates are -m<sup>2</sup> and MPa by 100-100,0001./. When the water transmission rate and the void content were in this range and this is used as an ionic exchanger of an electric type device for producing deionized water, it is desirable at the point of having satisfied both the intensity and desalting efficiency of the porous body. It is preferred that this polymeric material includes 10-90-mol% of a structure-of-cross-linkage unit to all the constitutional units which constitute a polymeric material using the organic polymer material in which the material of the skeletal part which forms an open cell has the structure of cross linkage. Since mechanical strengths run short that a structure-of-cross-linkage unit is less than [10 mol %], if 90-mol % is exceeded on the other hand undesirably, since introduction of an ion exchange group becomes difficult and ion exchange capacity falls, it is not desirable. There is no restriction in particular in the kind of this polymeric material, and For example, polystyrene, poly (alpha-methylstyrene), Styrene system polymer, such as polyvinylbenzyl

chloride; Polyethylene, Polyolefines, such as polypropylene; Nitrile system polymer, such as poly (halogenation olefin); polyacrylonitrile, such as polyvinyl chloride and polytetrafluoroethylene, Acrylic (meta) polymer, such as poly methyl methacrylate and ethyl polyacrylate; styrene divinylbenzene copolymer, a vinylbenzyl chloride divinylbenzene copolymer, etc. are mentioned. The above-mentioned polymer may be a copolymer from which even the homopolymer produced by polymerizing an independent monomer is obtained by polymerizing two or more monomers, and two or more kinds of polymer may be blended. In these organic polymer materials, styrene divinylbenzene copolymer and a vinylbenzyl chloride divinylbenzene copolymer are mentioned as a desirable material from the ease of introduction of an ion exchange group, and the height of a mechanical strength. The open cell structure of the porosity ionic exchanger of this invention can be observed comparatively easily with a SEM photograph.

[0015]As for the porosity ionic exchanger of this invention, an ion exchange group is distributed uniformly and the ion exchange capacity of more than 0.5 mg equivalents / g dry porous body is 2.0 mg equivalents / more than g dry porous body preferably. Since desalting efficiency falls that ion exchange capacity is less than 0.5 mg equivalents / g dry porous body, it is not desirable. Since it becomes uneven distributing the ion and electronic transition in a porosity ionic exchange of an ion exchange group uneven and reduction of electrical resistance and the efficient discharge to the enriching chamber of prehension ion become impossible, it is not desirable. Distribution of an ion exchange group says [ "the ion exchange group was distributed uniformly" and ] a uniform thing to mum order at least. The distributed situation of an ion exchange group can be checked comparatively easily by using EPMA, SIMS, etc. As an ion exchange group introduced into a porosity ionic exchanger, Cation exchange groups, such as a carboxylic acid group, an iminodiacetate group, a sulfonic group, a phosphate group, and a phosphoester group; A quaternary ammonium group, Anion exchange groups, such as the third class amino group, the second class amino group, a primary amino, polyethyleneimine, the third sulfonium group, and phosphonium group; dipolar ion exchange groups, such as a betaine and sulfobetaine, are mentioned.

[0016]The porosity ionic exchanger of this invention is what has the open cell structure where a macro pore group and the meso pore group of the specific opening which macro pore and macro pore overlap and produce exist uniformly, the conventional particle condensation type porous body is a completely different new structure, and holding the intensity of a porosity ionic exchanger, pore volume and specific surface area can be boiled markedly, and can be enlarged.

[0017]Especially as a manufacturing method of the above-mentioned porosity ionic exchanger, it is not restricted but the method of introducing an ion exchange group after that, etc. are mentioned by forming a porous body by the method of using as a porous body the ingredient containing an ion exchange group by a single step, and the ingredient which does not contain an ion exchange group. An example of the manufacturing method of a porosity ionic exchanger is shown below. That is, the porosity ionic exchanger concerned mixes a polymerization initiator [ the oil-soluble monomer, the surface-active agent, the water, and if needed ] which do not contain an ion exchange group, obtains a water-in-oil type emulsion, polymerizes this, and is manufactured.

[0018]As an oil-soluble monomer which does not contain an ion exchange group, excluding ion exchange groups, such as a carboxylic acid group, a sulfonic group, and a quaternary ammonium group, the solubility over water is low and points out an oleophilic monomer. As an example of these monomers, styrene, alpha-methylstyrene, Vinyltoluene, vinylbenzyl chloride, divinylbenzene, ethylene,

Propylene, isobutene, butadiene, isoprene, chloroprene, VCM/PVC, vinyl bromide, a vinylidene chloride, tetrafluoroethylene, Acrylonitrile, a methacrylonitrile, vinyl acetate, methyl acrylate, Ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, Trimethylolpropane triacrylate, butanediol diacrylate, Methyl methacrylate, ethyl methacrylate, methacrylic acid propyl, butyl methacrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, glycidyl methacrylate, ethylene glycol dimethacrylate, etc. are mentioned. These monomers can be independent one sort, or can be used combining two or more sorts. However, in this invention, cross-linking monomers, such as divinylbenzene and ethylene glycol dimethacrylate, are chosen as one ingredient of an oil-soluble monomer at least, It is desirable at the point that 15-80-mol the thing to consider as % faces the content preferably introducing many amounts of ion exchange groups at a next process 10-90-mol% among all the oil-soluble monomers, and a required mechanical strength is obtained. [0019] When a surface-active agent mixes the oil-soluble monomer and water which do not contain an ion exchange group, If a water-in-oil type (W/O) emulsion can be formed, there will be no restriction in particular, Sorbitan monooleate, sorbitan monolaurate, sorbitan monopalmitate, Sorbitan monostearate, sorbitan trioleate, polyoxyethylene nonylphenyl ether, Nonionic surface active agents, such as polyoxyethylene stearylether and polyoxyethylene sorbitan monooleate; Oleic acid potassium, Cationic surfactants, such as anionic surfactant; distearyldimethyl ammonium chloride, such as sodium dodecylbenzenesulfonate and dioctyl sodium sulfosuccinate; ampholytic surface active agents, such as a lauryldimethyl betaine, can be used. These surface-active agents can be independent one sort, or can be used combining two or more kinds. An oil phase turns into a continuous phase and a water-in-oil type emulsion means the emulsion which waterdrop is distributing in it. Since it changes substantially as an addition of the above-mentioned surface-active agent with the size of the emulsion particle (macro pore) made into the kind of oil-soluble monomer, and the purpose, it cannot generally say, but it can choose in about 2 to 70% of range to the total quantity of an oil-soluble monomer and a surface-active agent. In order to control the cellular shape and size of a porosity ionic exchanger, hydrocarbon, such as carboxylic acid; octane, such as alcoholic; stearic acid, such as methanol and stearyl alcohol, and a dodecane, can also be made to live together in a system, although it is not necessarily indispensable. [0020] As a polymerization initiator, the compound which generates a radical by heat and optical exposure is used suitably. A polymerization initiator may be water solubility, or may be oil solubility, and For example, azobisisobutyronitrile, Azobis cyclohexane nitril, azobis cyclohexanecarbonitrile, benzoyl peroxide, potassium persulfate, ammonium persulfate, hydrogen peroxide-ferrous chloride, sodium persulfate sodium hydrogen sulfite, tetramethylthiuramdisulfide, etc. are mentioned. However, even if it does not add a polymerization initiator depending on the case, the system of addition of a polymerization initiator in which a polymerization advances only by heating and optical exposure is also unnecessary for a certain reason by such a system. [0021]As a mixing method at the time of mixing the oil-soluble monomer, the surface-active agent, the water, and the polymerization initiator which do not contain an ion exchange group, and making a waterin-oil type emulsion form. There is no restriction in particular, and after carrying out the uniform dissolution of the oil-soluble ingredient which are the method, oil-soluble monomer and surface-active agent which bundle up each ingredient and are mixed at once, and an oil soluble polymerization initiator, and the water-soluble materials which are water and a water soluble polymerization initiator

independently, the method of mixing each ingredient, etc. can be used. There is no restriction in particular also about the mixed device for making an emulsion form, a usual mixer and homogenizer, a

high voltage homogenizer, etc. can be used, and what is necessary is just to choose a suitable device to obtain the target emulsion particle diameter. There is no restriction in particular also about mixing requirements, and the stirring number of rotations and mixing time which can obtain the target emulsion particle diameter can be set up arbitrarily.

[0022]Thus, the polymerization conditions which polymerize the obtained water-in-oil type emulsion can choose various conditions by the kind of monomer, and an initiator system. For example, when azobisisobutyronitrile, benzoyl peroxide, potassium persulfate, etc. are used as a polymerization initiator. In the hermetic container under an inert atmosphere, at 30-100 \*\*, 1 to 48 hours, What is necessary is just to make it polymerize at 0-30 \*\* in the hermetic container under an inert atmosphere for 1 to 48 hours, when what is necessary is just to have carried out the heating polymerization and hydrogen peroxide-ferrous chloride, sodium persulfate sodium hydrogen sulfite, etc. are used as an initiator. Contents are taken out after the end of a polymerization, a Soxhlet extraction is carried out with solvents, such as isopropanol, an unreacted monomer and a remains surface-active agent are removed, and a porous body is obtained.

[0023] As a method of introducing an ion exchange group into the porous body obtained by the polymerization process, there is no restriction in particular and publicly known methods, such as a polymeric reaction and graft polymerization, can be used. For example, as a method of introducing a sulfonic group. If a porous body is styrene divinylbenzene copolymer etc., chlorosulfuric acid and concentrated sulfuric acid, How to sulfonate using furning sulfuric acid; A radical start group and a chain transfer group are introduced into a porous body, How to carry out the graft polymerization of sodium styrenesulfonate or the acrylamide 2-methylpropanesulfonic acid; after carrying out the graft polymerization of the glycidyl methacrylate similarly, the method of introducing a sulfonic group by functional group conversion, etc. are mentioned. As a method of introducing a quaternary ammonium group, If a porous body is styrene divinylbenzene copolymer etc., after introducing a chloromethyl group with chloromethyl methyl ether etc., How to make react to the third class amine, and introduce; A porous body is manufactured by copolymerization of chloromethyl styrene and divinylbenzene, How to make react to the third class amine, and introduce; A radical start group and a chain transfer group are introduced into a porous body. How to carry out the graft polymerization of N.N.N-trimethylammonium ethyl acrylate or the N,N,N-trimethylammonium propylacrylamide; After carrying out the graft polymerization of the glycidyl methacrylate similarly, The method of introducing a quaternary ammonium group by functional group conversion, etc. are mentioned. As a method of introducing a betaine, after introducing the third class amine into a porous body by the above-mentioned method, the method of making monoiodoacetic acid react and introducing, etc. are mentioned. As an ion exchange group to introduce, a carboxylic acid group, an iminodiacetate group, Cation exchange groups, such as a sulfonic group, a phosphate group, and a phosphoester group; A quaternary ammonium group, Anion exchange groups, such as the third class amino group, the second class amino group, a primary amino, polyethyleneimine, the third sulfonium group, and phosphonium group; dipolar ion exchange groups, such as a betaine and sulfobetaine, are mentioned.

[0024]As a deionization module used for the electric type device for producing deionized water of this invention, For example, the cation exchange membrane 101 sealed in the porosity ionic exchanger 100 fabricated to tabular at one frame 103 side as shown in <u>drawing 1</u>, The deionization module 10A with which the building envelope 104 formed by the anion exchange membrane 102 sealed at the another side side is filled up, Or the cation exchange membrane 101 sealed in the porosity ionic exchanger 100a

fabricated to tabular at one frame 103a side as shown in drawing 2, The 1st building envelope 104a formed by the middle ion-exchange membrane 105 sealed between the frame 103a and the frame 103b is filled up, The deionization module 10B which fills up the 2nd building envelope 104b formed by the middle ion-exchange membrane 105 and the anion exchange membrane 102 sealed at the another side side of the frame 103b with the porosity ionic exchanger 100b fabricated to tabular is mentioned. Namely, the mode of the restoration to the deionization module of the porosity ionic exchanger of this invention, Especially if the purpose of deionized water manufacture is attained, it is not restricted, but the restoration mode which replaced the ionic exchanger in the conventional deionization module by the porosity ionic exchanger of this invention can be taken. Without using a frame, the deionization module of this invention can paste together and produce an ion-exchange membrane and a porosity ionic exchanger beforehand using adhesives etc., and can facilitate the assembling work of an electric type device for producing deionized water.

[0025] As an electric type device for producing deionized water of this invention, It has the abovementioned deionization module and the impurity ion the porosity ionic exchanger was made to catch is eliminated electrically, if it is a device which manufactures deionized water, it will not be restricted in particular but a monotonous type, cylindrical, and spiral type electric type device for producing deionized water will be mentioned. The desalting room where a monotonous type electric type device for producing deionized water is filled up with a porosity ionic exchanger between cation exchange membrane and anion exchange membrane, for example, The enriching chamber provided in the both sides of the desalting room via the above-mentioned cation exchange membrane and anion exchange membrane. A device and cation exchange membrane provided with the anode arranged at these both sides, and the negative pole, The 1st smallness desalting room formed by cation exchange membrane and the middle ion-exchange membrane arranged between anion exchange membrane, And the desalting room which fills up with a porosity ionic exchanger the 2nd smallness desalting room formed by this middle ion-exchange membrane and anion exchange membrane, respectively. Device \*\* provided with the enriching chamber provided in the both sides of the desalting room via the above-mentioned cation exchange membrane and anion exchange membrane, the anode arranged at these both sides, and the negative pole can be used. [0026] Hereafter, the electric type device for producing deionized water in an embodiment of the

invention is explained with reference to drawing 3. In drawing 3, 1 is a desalting room, 2 is an enriching chamber, and it is produced by constituting these desalting rooms 1 as above module articles. It fills up with this example so that the porosity dipolar ion exchanger 100c which introduced the dipolar ion exchange group may be inserted by the anion exchange membrane 102 and the cation exchange membrane 101, and it is considered as the deionization module 10A. The deionization module 10A is estranged and are installed side by side. [ two or more ] Between each deionization module 10A and 10A, the spacer (un-illustrating) which consists of watertight members, such as rubber packing formed in frame shape, intervenes, and the space part formed by doing in this way is constituted as the enriching chamber 2. The anode 110 and the negative pole 109 are arranged to the side part of the mutual alignment body of the desalting room 1 and the enriching chamber 2, The partition films 113 and 114 are formed near the anode 110 is made into the positive pole room 111, and the space part between this partition film 113 and the negative pole 109 is constituted as the cathode room 112. Although the porosity dipolar ion exchanger 100c, and the anion exchange membrane 102 and the cation exchange

membrane 101 which are located in the both sides are estranged with the relation of a graphic display in drawing 3, the porosity dipolar ion exchanger 100c, and the anion exchange membrane 102 and the cation exchange membrane 101 are stuck in practice. The porosity ionic exchanger and ion-exchange membrane which form a desalting room also in drawing 4 mentioned later - drawing 7 are stuck. [0027]The electric type device for producing deionized water of drawing 3 is operated as follows. First, processed water is flowed in the desalting room 1, and retentate is flowed in the enriching chamber 2, and electrode water is flowed into the positive pole room 111 and the cathode room 112, respectively. The thing usually same as retentate as the processed water supplied to the desalting room 1 is used. On the other hand, voltage is impressed between the anode 110 and the negative pole 109, and a direct current is led to rectangular directions to the flow direction of processed water and retentate. When the processed water which flowed in the desalting room 1 circulates the inside of the open cell structure which consists of the macro pore and meso pore of a porosity ionic exchanger, ion is caught by the ion exchange group introduced in this open cell structure, and this ion is eliminated in the enriching chamber 2 through the ion-exchange membranes 101 and 102.

[0028] The electric type device for producing deionized water of other embodiments is shown in drawing 4 - drawing 7. The number of deionization modules is suitably determined by service conditions, such as throughput, and a deionization module is displayed for the purpose of the simplification of a drawing in drawing 4 - drawing 7 at two pieces. Identical codes are given to an identical configuration element, the explanation is omitted and a different point is mainly explained. The deionization module 10A which a different point from drawing 3 has in the point of having changed the kind of porosity ionic exchanger which constitutes a deionization module, in drawing 4, and is used with the device of drawing 4, The porosity dipolar ion exchanger 100c which introduced the dipolar ion exchange group, 100 d of porosity cation exchangers which introduced the cation exchange group. The porosity anion exchanger 100e which introduced the anion exchange group is manufactured in the shape of a small block, respectively, From the inflow side of processed water, the porosity dipolar ion exchanger 100c, 100 d of porosity cation exchangers, It is the mode constituted so that it might laminate so that it may become the porosity anion exchanger 100e, 100 d of porosity cation exchangers, and the porosity anion exchanger 100e, and this might be inserted by the anion exchange membrane 102 and the cation exchange membrane 101. [0029]The deionization module 10A which a different point from drawing 3 has in the point of having changed the kind of porosity ionic exchanger which constitutes a deionization module, in drawing 5, and is used with the device of drawing 5, Making the porosity ionic exchanger side 100 d of porosity cation exchangers and the porosity anion exchanger 100e contact mutually, an applicable plane of composition is the mode constituted so that the both sides of an opposite hand might be inserted by the anion exchange membrane 102 and the cation exchange membrane 101.

[0030]In drawing 6, a different point from drawing 3 connects in series the point and two deionization modules into which the kind of porosity ionic exchanger which constitutes a deionization module was changed, and is one of the points which used the effluent of one deionization module as the processed water of the deionization module of another side. Namely, the deionization module 10A used with the device of drawing 6, It is filled up so that 100 d of porosity cation exchangers which introduced the cation exchange group, and the porosity anion exchanger 100e which introduced the anion exchange group may be inserted by the anion exchange membrane 101,

respectively, Make each into decation module  $10A_1$  and deanion module  $10A_2$ , and let the effluent of deanion module  $10A_3$  be processed water of decation module  $10A_4$ .

[0031]Each deionization module used with the device of <u>drawing 3</u> - <u>drawing 6</u> can use the deionization module 10A shown in drawing 1.

[0032]On the other hand, the deionization module 10B shown in drawing 2 can be used for the deionization module used with the device of drawing 7. Namely, the two small desalting rooms 1a where the device of drawing 7 is divided by the middle ion-exchange membrane 105 located between the cation exchange membrane 101 by the side of one, the anion exchange membrane 102 by the side of other and the cation exchange membrane 101, and the anion exchange membrane 102. To the small desalting room 1b by the side of the cation exchange membrane 101 of 1b, a porosity dipolar ion exchanger, Or it is filled up with 100 f of layered products of a porosity anion exchange rand a porosity cation exchanger, Fill up the small desalting room 1a by the side of the anion exchange membrane 102 with the porosity anion exchanger 100e, and the desalting room 1 is constituted. The enriching chamber 2 is formed in the both sides of a desalting room via the cation exchange membrane 101 and the anion exchange membrane 102, and these desalting rooms 1 and enriching chambers 2 are arranged between the anode 110 and the negative pole 109, and it is constituted. In this example, the middle ion-exchange membrane 105 is using anion exchange membrane.

[0033] The electric type device for producing deionized water of drawing 7 is operated as follows. First, it flows in the small desalting room 1a, processed water is ranked second, it flows into other small desalting rooms 1b which adjoin the effluent of the small desalting room 1a, and retentate is flowed in the enriching chamber 2, and electrode water is flowed into the positive pole room 111 and the cathode room 112, respectively. The thing usually same as retentate as the processed water supplied to the small desalting room 1a is used. On the other hand, voltage is impressed between the anode 110 and the negative pole 109, and a direct current is led to rectangular directions to the flow direction of processed water and retentate. Ion is caught by the ion exchange group introduced in this open cell structure, and the processed water which flowed in the small desalting room 1a is removed, when circulating the inside of the open cell structure which consists of the macro pore and meso pore of the porosity anion exchanger 100e. When the effluent of the small desalting room 1a circulates the inside of the open cell structure which consists of the macro pore of 100 f of layered products and meso pore of a porosity dipolar ion exchanger or a porosity anion exchanger, and a porosity cation exchanger, Ion is caught and removed by the ion exchange group introduced in this open cell structure. Retentate goes up each enriching chamber, receives the impurity ion which moves via the cation exchange membrane 101 and the anion exchange membrane 102, and is discharged out of a system as retentate which condensed impurity ion.

[0034]

[Example]Next, although an example is given and this invention is explained still more concretely, this is only illustration and does not restrict this invention.

27.7 g of example 1 (manufacture of a porosity cation exchanger) styrene, 6.9 g of divinylbenzene, 0.14g of azobisisobutyronitrile, and 3.8 g of sorbitan monooleate were mixed, and it was made to dissolve uniformly. Next, the styrene / divinylbenzene / azobisisobutyronitrile / the sorbitan monooleate mixture concerned were added to 450 ml of pure water, it stirred for 2 minutes by 20,000 revolutions per minute using the homogenizer, and the water-in-oil type emulsion was obtained. The water-in-oil type

emulsion was moved to the autoclave made from stainless steel after the end of emulsification, after nitrogen replaced enough, it sealed, and it was made to polymerize at 60 \*\* under settlement for 24 hours. After having taken out contents after the end of a polymerization, carrying out the Soxhlet extraction by isopropanol for 18 hours and removing an unreacted monomer and sorbitan monooleate, reduced pressure drying was carried out at 40 \*\* one whole day and night, thus, the bridge construction ingredient which consists of obtained styrene / a divinylbenzene copolymer -- 14-mol % -- after isolating 5 g of contained porous bodies preparatively, adding 500 g of tetrachloroethane and heating at 60 \*\* for 30 minutes, it cools to a room temperature, and the chlorosulfuric acid 25g was added gradually and made to react at a room temperature for 24 hours Then, acetic acid was added, the reactant was supplied to underwater [a lot of], it rinsed and dried and the porosity cation exchanger was obtained. The ion exchange capacity of this porous body is 4.0 mg equivalents / g in dry porous body conversion. By mapping of the sulfur atom using EPMA, it checked that the sulfonic group was uniformly introduced into the porous body.

The internal structure of this porous body has open cell structure as a result of the SEM observation shown in drawing 8.

The average value of the diameter of the meso pore which the great portion of macro pores with a pitch diameter of 30 micrometers overlap, and is formed by the lap of macro pore and macro pore is 5 micrometers. Whole pore volume was  $10.1 \text{ m/y}_s$ .

When the above-mentioned porous body was started in thickness of 10 mm and the water transmission rate was measured, it is  $-\mathrm{m}^2$  and MPa by 14,000L/, and good water permeability was shown. [0035]Instead of 27.7 g of example 2 (manufacture of a porosity anion exchanger) styrene, Using 18.0 g of p-chloromethyl styrene, 17.3 g of divinylbenzene, the bridge construction ingredient which polymerizes the same water-in-oil type emulsion as Example 1, and consists of p-chloromethyl styrene / a divinylbenzene copolymer except having considered it as 0.26 g of azobisisobutyronitrile -- 50-mol % -- the contained porous body was manufactured. 5 g of this porous body was isolated preparatively, after adding the dioxane 500g and heating at 80 \*\* for 30 minutes, it cooled to the room temperature, and after adding the trimethylamine (30%) solution 65g gradually and making it react at 50 \*\* for 3 hours, it allowed to stand at the room temperature one whole day and night. The porous body was taken out after ending reaction, and with acetone, it rinsed after washing, it dried, and the porosity anion exchanger was obtained. The ion exchange capacity of this porous body is 2.5mg equivalents/g in dry porous body conversion.

By SIMS, it checked that the trimethylammonium group was uniformly introduced into the porous body. The internal structure of this porous body has open cell structure as a result of SEM observation. The average value of the diameter of the meso pore which the great portion of macro pores with a pitch diameter of 30 micrometers overlap, and is formed by the lap of macro pore and macro pore is 4 micrometers. Whole pore volume was 9.9ml/g.

micrometers. Whole pore volume was 9.9ml/g. When the above-mentioned porous body was started in thickness of 10 mm and the water transmission rate was measured, it is -m² and MPa by 12,000l./, and good water permeability was shown. [0036]It replaced with 0.14 g of comparative example 1 azobisisobutyronitrile, and except having changed having used the potassium persulfate 0.60g and the amount of 3.8 g of the sorbitan monooleate used into 15.5 g, the same operation as Example 1 was performed, and the porosity cation exchanger was obtained. Although ion exchange capacity was [4.0mg equivalents/g, and whole pore volume ] 9.2 ml/g in dry porous body conversion, its average value of the diameter of meso pore was as small as 0.2

micrometer, and when the obtained porous body measured the water transmission rate like Example 1, they were  $-m^2$  and MPa by 401./.

[0037]The porosity cation exchanger, porosity anion exchanger, and porosity dipolar ion exchanger which were obtained in example 3 (production of a deionization module) Examples 1 and 2 were cut in 100 mm long, 100 mm wide, and an 8-mm-wide size, and it was considered as five small blocks, respectively. Namely, the porosity dipolar ion exchanger 100c, 100 d of porosity cation exchangers, The porosity anion exchanger 100e is manufactured in the shape of a small block, respectively. From the inflow side of processed water, the porosity dipolar ion exchanger 100c, 100 d of porosity cation exchangers, It laminated so that it might become the porosity anion exchanger 100e, 100 d of porosity cation exchangers, and the porosity anion exchanger 100e, it was filled up so that this might be inserted by the anion exchange membrane 102 and the cation exchange membrane 101, and a deionization module which is used with the device of drawing 4 was obtained.

[0038]The electric type device for producing deionized water was manufactured by making into a desalting room the deionization module obtained example 4 (manufacture and operation of an electric type device for producing deionized water). The electric type device for producing deionized water was used as the device which consists of one desalting room, one positive pole room, and one cathode room. Between the desalting room and the positive pole room, between the desalting room and the cathode room, the spacer was inserted, respectively, and the enriching chamber was formed. To this electric type device for producing deionized water, the conductivity which processed the city water by the reverse osmotic membrane supplied the water of 3.6microS/cm as processed water, and it operated to it. By the operation current 0.40Å of the electric type device for producing deionized water, the treated water of specific resistance 5.0M omegacm was obtained. The operation voltage at this time was 20V. [0039] It replaced with the porosity ionic exchanger of comparative example 2 open-cell structure, and the electric type device for producing deionized water was operated on the same conditions as Example 4 except having used what carried out equivalent mixing of Amberlite 120B and the Amberlite 402BL. To this electric type device for producing dejonized water, the conductivity which processed the city water by the reverse osmotic membrane supplied the water of 3.6microS/cm as processed water, and it operated to it. By the operation current 0.40A of the electric type device for producing deionized water, the treated water of 5.0 M omega of specific resistance cm was obtained. The operation voltage at this time was 30V.

[0040]Example 4 has checked that the operation voltage of an electric type device for producing deionized water was reduced, and power consumption could be saved by using an ionic exchanger as a porosity ionic exchanger as contrasted with the comparative example 2. While the production of the deionization module had to fill up ion-exchange resin with the comparative example 1 uniformly according to the damp or wet condition and pains was taken over manufacture, there was no work of uniform restoration of ion-exchange resin at Examples 3 and 4, and it was easy.

[0041]

[Effect of the Invention]The porosity ionic exchanger of this invention is an ionic exchanger with a specific open cell structure.

The conventional particle condensation type porous body is a completely different new structure. this especially porous body holding intensity, pore volume and specific surface area can be boiled markedly, and it can enlarge them. According to the deionization module of this invention, since it can fabricate cylindrical and cutting can use plate-like and an easy polymer material, the porosity ionic

exchanger with which the space between ion-exchange membranes is filled up is easy to assemble, and it can make it a simple structure, for example. Since the electric type device for producing deionized water of this invention has high desalting efficiency, it can reduce the voltage at the time of operation, and can be used as the power-saving type which can reduce power consumption.

[Translation done.]